

Electronic Supplementary Information

Development of a Ru–porphyrin-based supramolecular framework catalyst for styrene epoxidation

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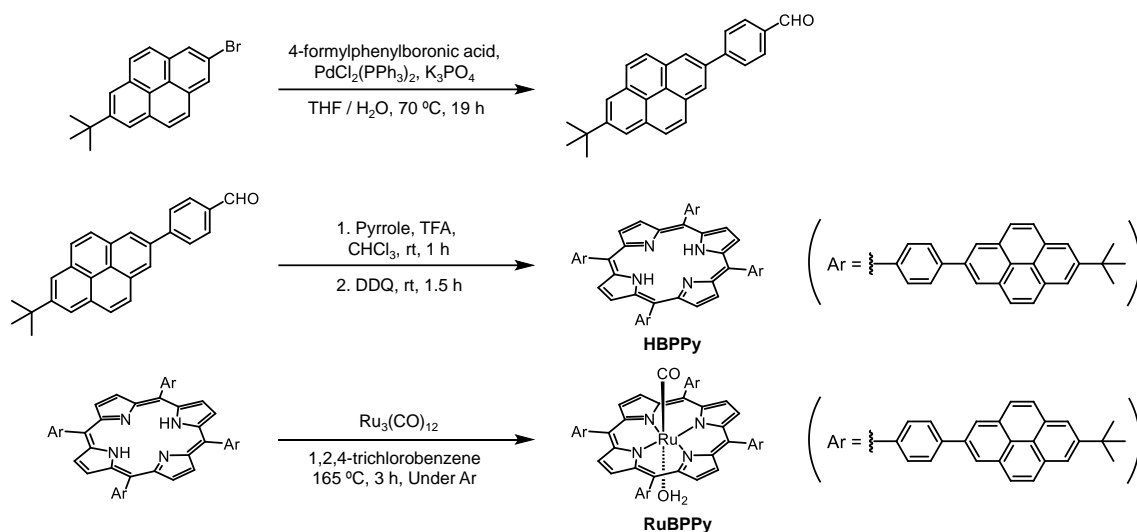
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1. Experimental details

General procedures

Pyrrole, sodium borohydride, 1-methyl-2-pyrrolidone (NMP) and Triruthenium dodecacarbonyl ($\text{Ru}_3\text{CO}_{12}$) were purchased from Sigma-Aldrich Co., LLC. *p*-formylphenylboronic acid, tripotassium phosphate bis(triphenylphosphine)palladium(II) dichloride, diethyl ether, ferrocene, trifluoroacetic acid (TFA), 1,2,4-trichlorobenzene, hydrogen peroxide, sodium carbonate, sodium sulfate, hexane, cyclohexane, benzene and Chloroform- d_1 (CDCl_3) were purchased from Wako Pure Chemical Industries, Ltd. Methanol, chloroform (CHCl_3), tetrahydrofuran (THF), *o*-dichlorobenzene (*o*-DCB), acetonitrile (MeCN), ethanol and acetone were purchased from Kanto Chemical Co., Inc. 2-bromo-7-tert-butylpyrene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 2,6-dichloropyridine were purchased from Tokyo Chemical Industry Co., Ltd. All solvents and reagents are of the highest quality available and used as received. NMR spectra were collected at room temperature on a JEOL JNM-ECS400 spectrometer. Elemental analysis was performed on a J-SCIENCE LAB MICRO CORDER JM10 elemental analyzer. UV-visible spectra were recorded on a Shimadzu UV-3600 UV-vis-near-IR spectrophotometer. Diffuse-reflectance UV-visible spectrum was recorded on a Shimadzu UV-3600i Plus UV-vis-NIR spectrophotometer. A white standard of BaSO_4 was used as the reference for diffuse-reflectance spectroscopic measurements. FT-IR spectrum was recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Powder X-ray diffraction data were collected on a Rigaku MiniFlex600. The CO_2 adsorption isotherms at 195 K were measured using a BELSORP-max volumetric adsorption analyzer from MicrotracBEL Corp. The temperature was adjusted using a cryostatic temperature controller from ULVAC CRYOGENICS INC. The sample was dried under a dynamic vacuum at 373 K for 16 h prior to the measurement.

2. Synthesis



Scheme S1. Synthetic scheme for **RuBPPy**.

Synthesis of 4-(7-(tert-butyl)pyren-2-yl)benzaldehyde

4-(7-(tert-butyl)pyren-2-yl)benzaldehyde was synthesized as previously reported.^{S1} $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.13 (s, 1H), 8.40 (s, 2H), 8.25 (s, 2H), 8.11 (s, 4H), 8.06 (s, 4H), 1.60 (s, 9H) ppm.

Synthesis of 5,10,15,20-tetrakis(4-(7-(tert-butyl)pyren-2-yl)phenyl)porphyrin (HBPPy)

HBPPy was synthesized as previously reported.^{S2} $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 9.10 (s, 8H), 8.74 (s, 8H), 8.48 (d, J = 8.0 Hz, 8H), 8.34 (d, J = 7.6 Hz, 8H), 8.29 (s, 8H), 8.25 (d, J = 9.2 Hz, 8H), 8.17 (d, J = 8.8 Hz, 8H), 1.63 (s, 36H), -2.55 (s, 2H) ppm. λ_{max} (CHCl_3)/nm 312 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 8600), 326 (13000), 342 (19000), 425 (600000), 519 (22000), 556 (17000), 593 (7500), 649 (7300).

Synthesis of aquacarbonyl{5,10,15,20-tetrakis(4-(7-(tert-butyl)pyrene-2-yl)phenyl)porphyrinato}-ruthenium(II) (RuBPPy)

RuBPPy was synthesized by modifying a previous report.^{S3} A 50-mL schlenk was charged with 1,2,4-trichlorobenzene (10 mL), followed by degassing with argon for 15 min. After that, **HBPPy** (78.6 mg) was added to the degassed solution under argon. The reaction system was then purged continuously with argon and heated to 165 °C. 5 portions of $\text{Ru}_3(\text{CO})_{12}$ (15.7 mg each, total 78.6 mg) were added to the reaction mixture (protected with argon flow) at a 15-minute interval. After the addition of the final portion, the mixture was allowed to stir for an extra 1 h. The reaction mixture was then cooled to room temperature and filtered to remove unreacted $\text{Ru}_3(\text{CO})_{12}$. The filtrate was purified through silica gel column chromatography with CHCl_3 . The eluent containing 1,2,4-trichlorobenzene was obtained and concentrated under vacuum. The red precipitate was obtained by pureeing the solution into MeCN

(300 mL) and filtration. Recrystallization by the slow evaporation using an evaporator (40 °C, 285 hpa) of a mixed solvent of chloroform and acetonitrile (2:1) gave the dark red solid (52 mg, 60%). ¹H-NMR (400 MHz, CDCl₃) δ = 8.95 (s, 8H), 8.74 (s, 8H), 8.37-8.50 (m, 8H), 8.30-8.37 (m, 8H), 8.29 (s, 8H), 8.20-8.27 (m, 8H), 8.11-8.20 (d, *J* = 8.8 Hz, 8H), 1.63 (s, 36H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 149.36, 144.38, 141.70, 140.73, 138.32, 134.70, 132.18, 131.75, 131.18, 128.27, 127.67, 126.36, 124.21, 123.87, 123.02, 122.65, 121.91, 35.46, 32.13 ppm. Elemental analysis Calcd. for C₁₂₅H₉₄N₄O₂Ru · H₂O (**RuBPPy** · H₂O): C, 83.26%; H, 5.37%; N, 3.11%. Found: C, 83.08%; H, 5.44%; N, 3.20%. λ_{max} (CHCl₃)/nm 312 (ε/dm³ mol⁻¹ 9900), 326 (14000), 342 (19000), 418 (350000), 532 (29000), 566 (8800).

Synthesis of 2,6-dichloropyridine *N*-oxide

2,6-dichloropyridine *N*-oxide was synthesized as previously reported.^{S4} ¹H NMR (400 MHz, CDCl₃): δ = 7.12 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H) ppm.

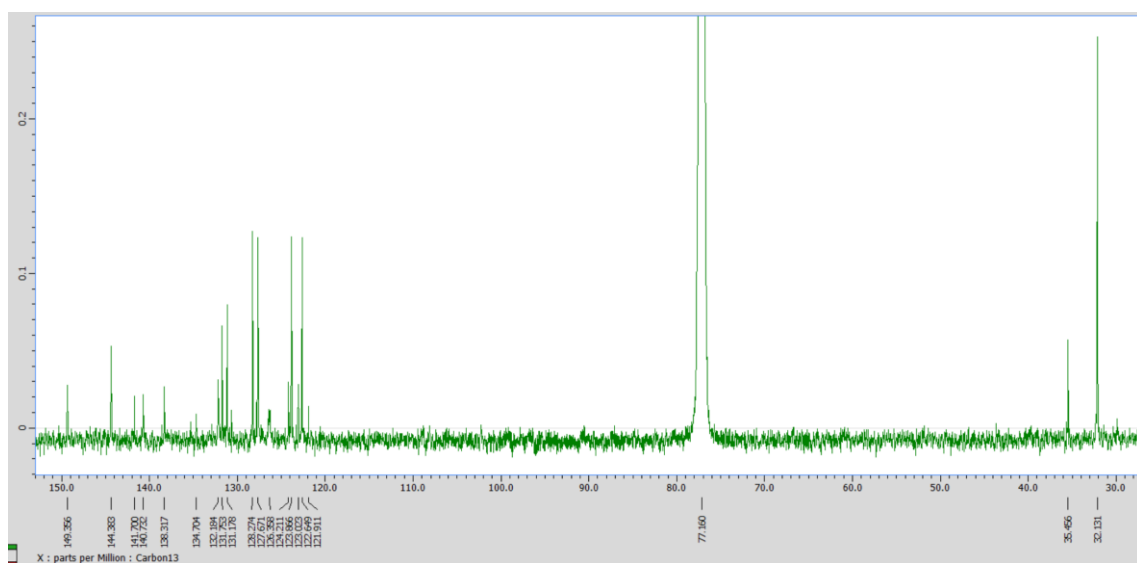


Fig. S2. ^{13}C NMR spectrum of **RuBPPy**.

3. Physical properties

3.1 UV-vis Absorption Spectroscopy

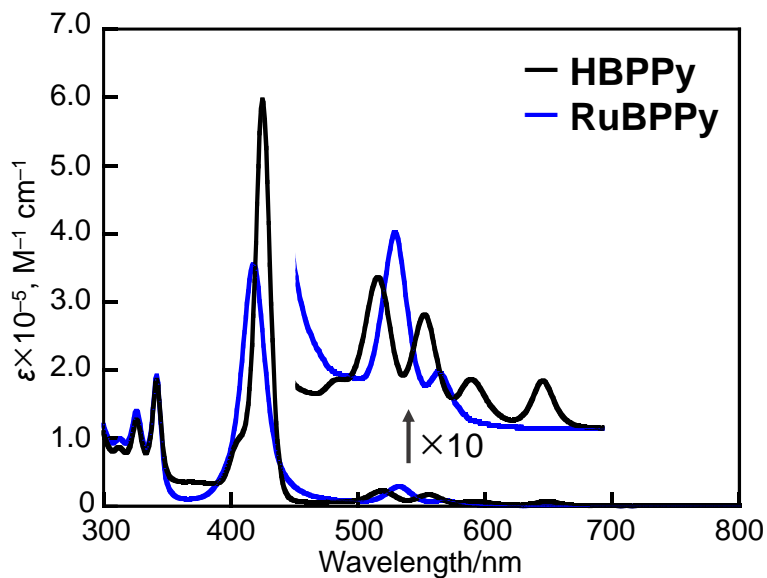


Fig. S3. UV-vis absorption spectra of **HBPPy** and **RuBPPy** in CHCl_3 .

Table S1. Summary of the absorption spectra for **HBPPy** and **RuBPPy** in CHCl_3

Compound	$\lambda_{\text{max}}/ \text{nm}$		
	Substituent's bands	Soret band	Q-bands
HBPPy	312, 326, 342	425	519, 556, 593, 649
RuBPPy	312, 326, 342	418	532, 566

3.2 Physical properties of [RuBPPy]_{FC}

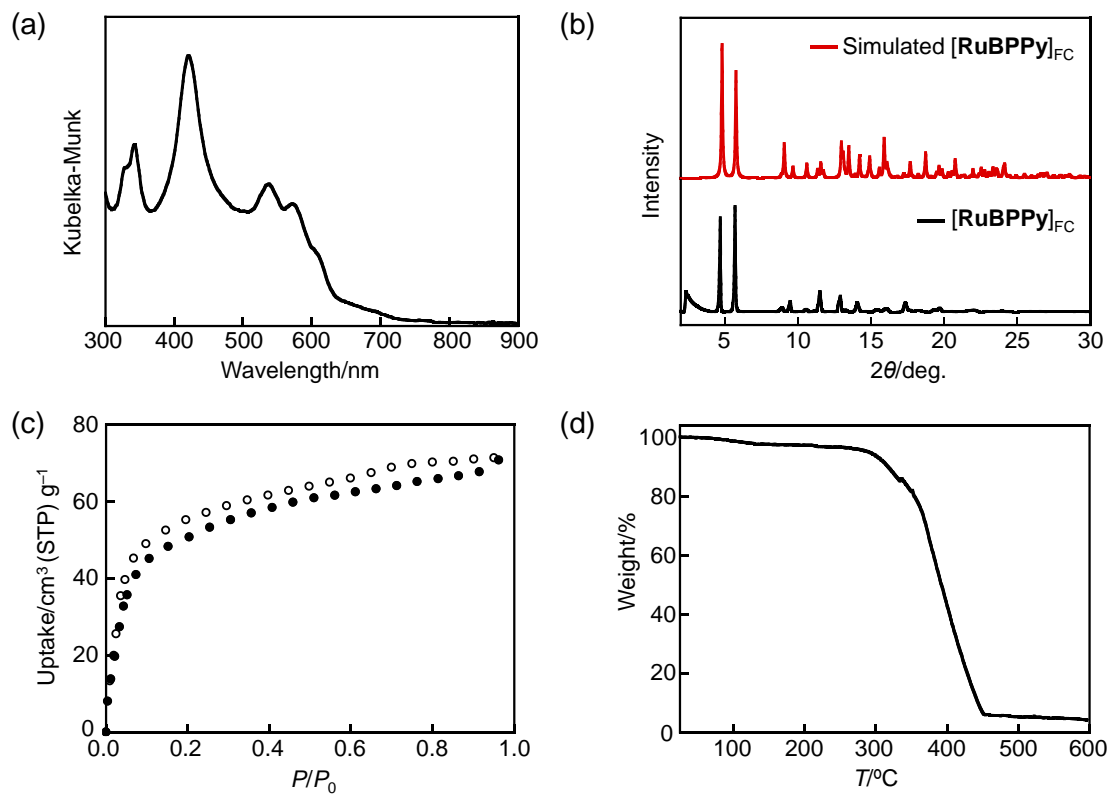


Fig. S4 (a) Diffuse-reflectance UV-vis spectrum of [RuBPPy]_{FC}. (b) Experimental and simulated PXRD patterns for [RuBPPy]_{FC}. (c) Adsorption and desorption isotherms of CO₂ for [RuBPPy]_{FC} at 195 K. (d) TGA curve of [RuBPPy]_{FC} within 25–600 °C under N₂.

3.3 FT-IR spectroscopy

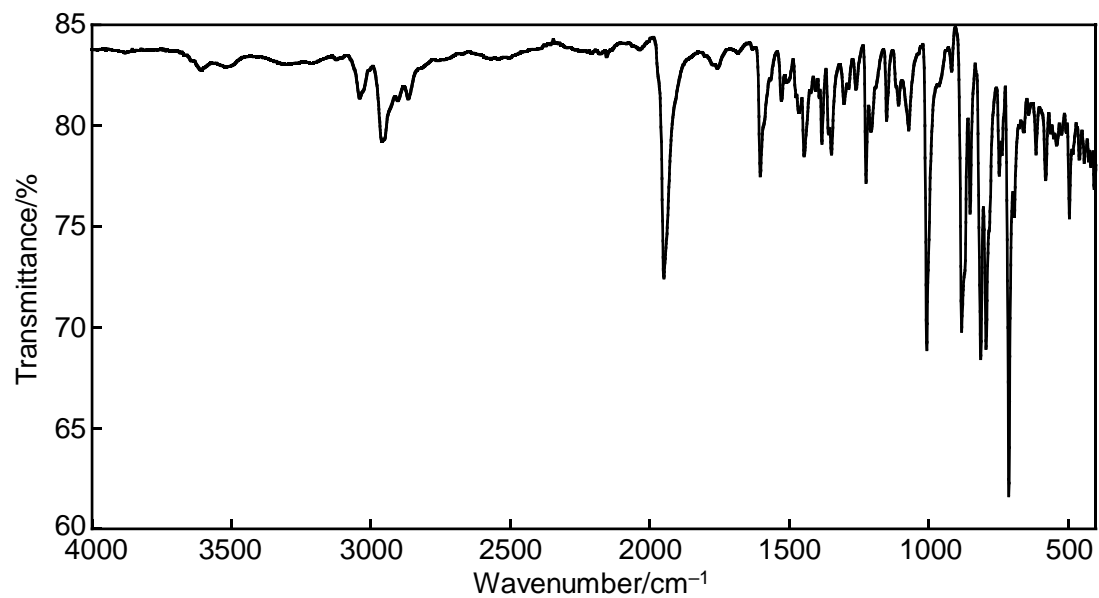


Fig. S5. FT-IR spectrum of [RuBPPy]_{FC}.

4. Electrochemical measurement

Cyclic voltammetry was performed with a Bio-Logic-Science Instruments potentiostat interfaced to a computer with SP-50 software, at room temperature under Ar using a one-compartment cell with a standard three-electrode configuration, which consisted of a glassy carbon disk (diameter 3 mm, BAS Inc.), a Ag/Ag⁺ couple, and a platinum wire as the working, reference and auxiliary electrodes, respectively. The working electrode was treated between scans using polishing with 0.05 μm alumina paste (BAS Inc.) and washing with purified H₂O. Ferrocene was used as an internal standard, and all potentials reported within this work are referenced to the ferrocenium/ferrocene couple at 0 V.

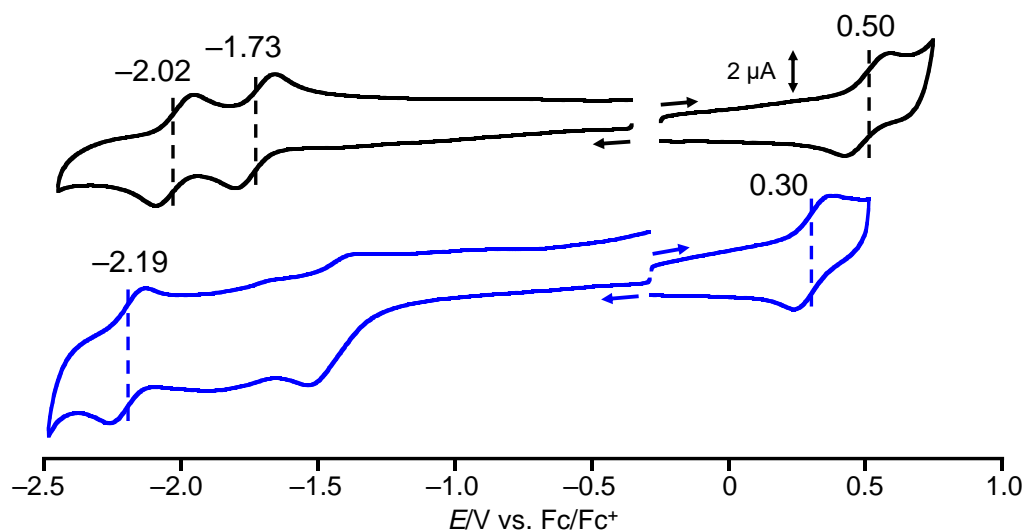


Fig. S6. Cyclic voltammograms of **HBPPy** (0.2 mM, black) and **RuBPPy** (0.2 mM, blue) in *o*-DCB with TBAP (0.1 M) under Ar. WE: GC, RE: Ag/Ag⁺, CE: Pt wire, Scan rate: 100 mV s⁻¹.

5. Single-crystal X-ray structural analysis

Single crystal X-ray diffraction data were collected on a Synergy Custom system CCD Plate equipped with confocal monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) coated with Paratone-N (Hampton Research Corp., Aliso Viejo, CA, USA). Data was processed using CrysAlisPro system software.^{S5} The structures were solved by a dual-space algorithm using SHELXT program^{S6} through the Olex2 interface.^{S7} All non-hydrogen atoms were refined anisotropically using a least-squares method, and hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXL-2014/7 was used for structure refinement.^{S8} Full-matrix least-squares refinements on F^2 based on unique reflections with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($I > 2.00 \sigma(I)$) and $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ were performed. *PLATON-SQUEEZE*^{S9} was performed for **[RuBPPy]_{as-syn}** and, 121 electrons were found per unit cell. This is consistent with the presence of one CHCl₃ molecule per asymmetric unit which accounts for 116 electrons per unit cell. Mercury 4.2.0 was used for visualization and analysis of the structure. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 2368114 for **[RuBPPy]_{FC}** and 2368115 for **[RuBPPy]_{as-syn}**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

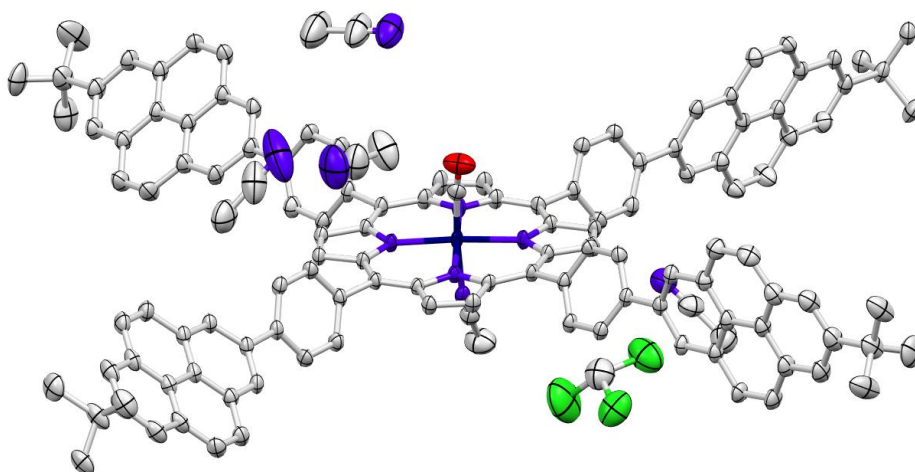


Fig. S7. An ORTEP drawing of **[RuBPPy]_{as-syn}** (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. C = gray, N = blue, O = red, and Ru = dark blue.

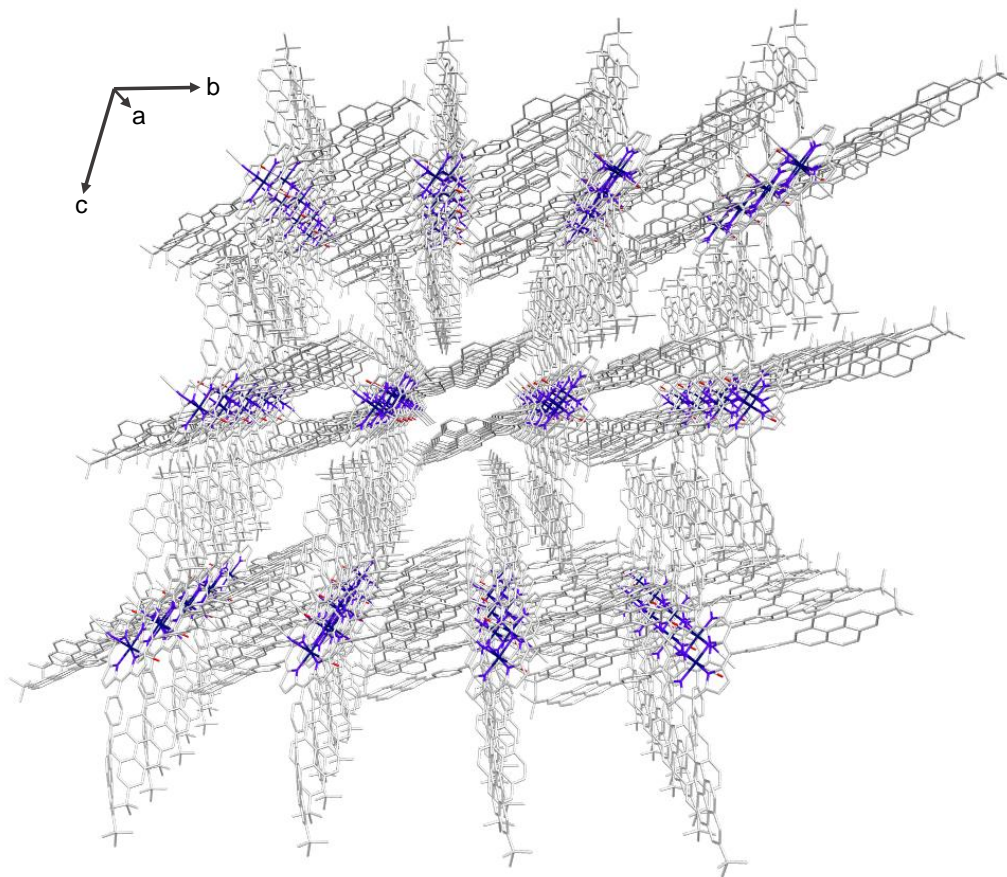


Fig. S8. Packing structure of $[\text{RuBPPy}]_{\text{as-syn}}$. Crystal solvents are omitted for clarify.

Table S2. Summary of crystallographic data for [RuBPPy]_{as-syn}

formula	C ₁₃₆ H ₁₀₈ Cl ₃ N ₉ ORu
formula weight	2091.73
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	15.3821(2)
<i>b</i> , Å	16.7184(4)
<i>c</i> , Å	23.3719(3)
<i>α</i> , deg	102.612(2)
<i>β</i> , deg	104.1350(10)
<i>γ</i> , deg	93.6510(10)
<i>V</i> , Å ³	5644.16(18)
<i>Z</i>	2
ρ_{calc} , g/cm ³	1.231
<i>F</i> (000)	2180.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
2 θ_{max} , deg	62.618
reflns measd	95711
uniq reflns	30950
<i>R</i> (int)	0.0455
data/restraints/params	30950/0/1399
<i>R</i> ₁	0.0820
w <i>R</i> ₂	0.2286
<i>GOF</i>	1.054

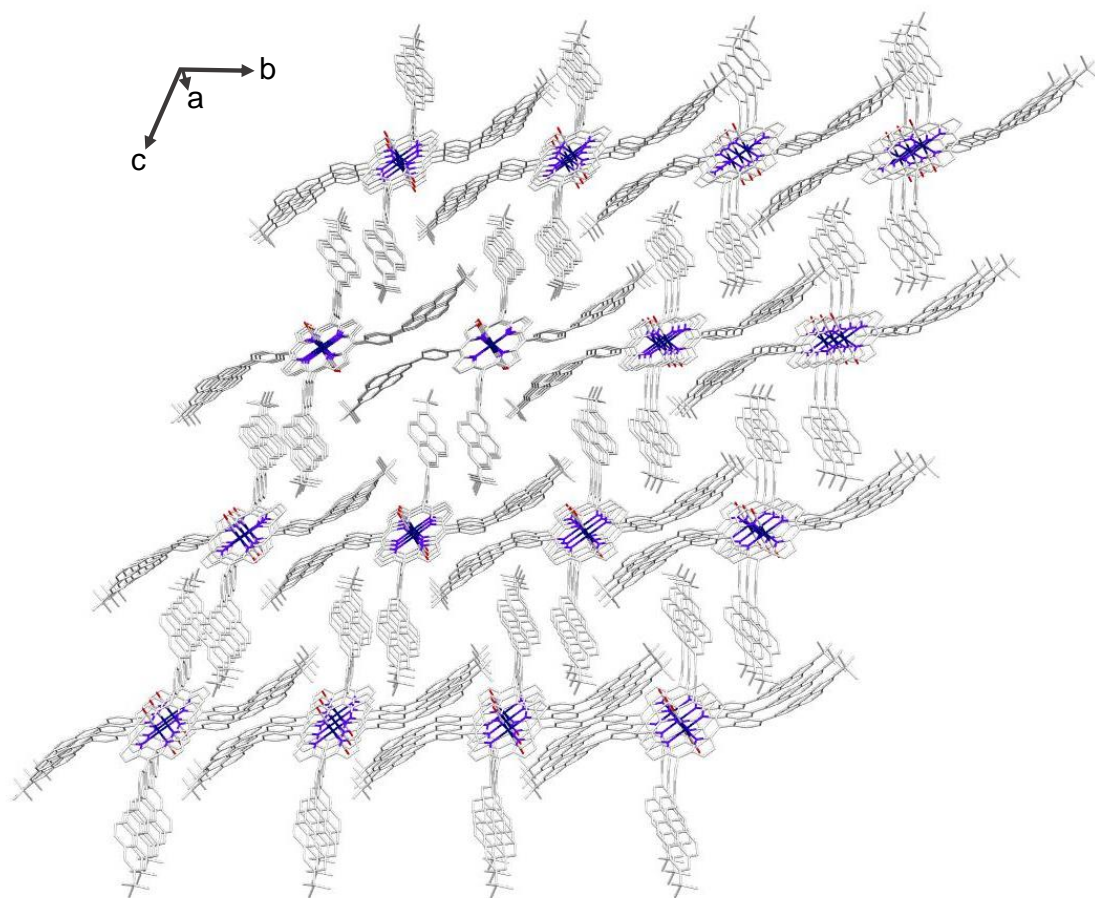


Fig. S9. Packing structure of [RuBPPy]_{FC}.

Table S3. Summary of crystallographic data for [RuBPPy]_{FC}

formula	C ₁₂₅ H ₉₂ N ₄ O ₂ Ru
formula weight	1783.09
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	7.8860(6)
<i>b</i> , Å	16.7298(10)
<i>c</i> , Å	19.9827(10)
<i>α</i> , deg	112.717(5)
<i>β</i> , deg	94.736(5)
<i>γ</i> , deg	95.806(5)
<i>V</i> , Å ³	2398.0(3)
<i>Z</i>	1
ρ_{calc} , g/cm ³	1.235
<i>F</i> (000)	930.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
$2\theta_{\text{max}}$, deg	50.106
reflns measd	26456
uniq reflns	8493
<i>R</i> (int)	0.1580
data/restraints/params	8493/25/604
<i>R</i> ₁	0.0638
w <i>R</i> ₂	0.1149
<i>GOF</i>	0.948

Table S4. Summary of the averaged Ru–N bond distances^a of Ru–porphyrins

Complex	Averaged Ru–N bond distance ^b /Å	Reference
[RuBPPy]_{as-syn}	2.054(3)	This work
[RuBPPy]_{FC}	2.052(3)	This work
[Ru(II)(TPP)(CO)(H ₂ O)] ^c	2.045(3)	S10
[Ru(II)(TPP)(CO)(EtOH)]	2.049(5)	S11
[Ru(II)(F ₂₀ -TPP)(CO)(H ₂ O)] ^d	2.055(3)	S12
[Ru(II)(TMTTP)(CO)(H ₂ O)] ^e	2.070(4)	S13
[Ru(III)(TPP)(OEt)(EtOH)]	2.040(6)	S14
[Ru(III)(2,6-Cl ₂ TPP)(Ph)(OEt ₂)] ^f	2.031(4)	S15
[Ru(III)(2,6-Cl ₂ TPP)(Ph)(H ₂ O)]	2.034(14)	S15
[Ru(III)(2,6-Cl ₂ TPP)(Cl)(THF)]	2.041(4)	S15
[Ru(IV)(TMP)(Cl) ₂] ^{g, h}	2.024(9), 2.034(6)	S16
[Ru(IV)(2,6-Cl ₂ TPP)(Cl) ₂]	2.040(7)	S16

^aThe distances between Ru atom and N atom of porphyrin ring, ^bThe distance with standard deviation, ^cTPP = tetraphenylporphyrinato dianion, ^dF₂₀-TPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato dianion, ^eTMTTP = 1,3,5,7-tetramethyl-2,4,6,8-tetraterphenylporphyrinato dianion, ^f2,6-Cl₂TPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato dianion, ^gTMP = *meso*-tetramesitylporphyrinato dianion. ^hThere are two types of independent molecules in the unit cell.

6. Powder X-ray diffraction

The crystalline powder of [RuBPPy]_{FC} is soaked in a solvent for 2 h. The powder was collected by filtration and dried at room temperature *in vacuo*, the powder X-ray diffraction data was collected.

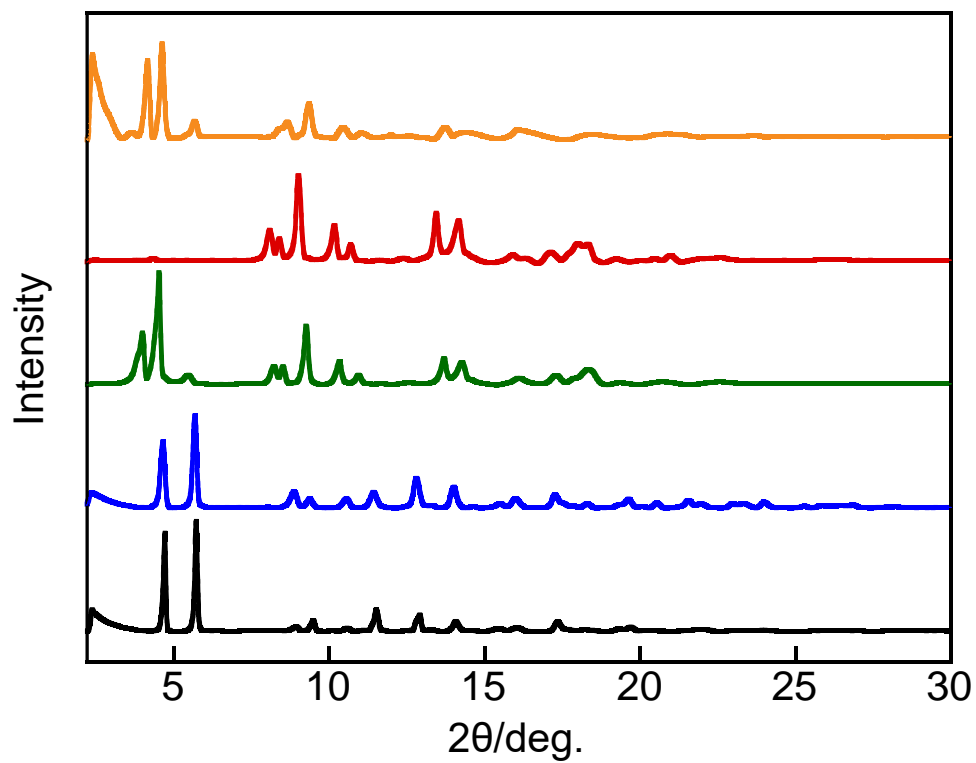


Fig. S10. PXRD patterns for [RuBPPy]_{FC} (black), after soaking in acetonitrile (blue), hexane (green), cyclohexane (red) and 5.0% benzene in cyclohexane (orange) for 2 h and drying.

7. Photochemical epoxidation of styrene

7.1 Standard conditions and experimental setup

For the typical run, 5.0% benzene in cyclohexane (2.0 mL) solution containing 43 mM styrene was added to [RuBPPy]_{FC} (260 μg, 0.14 μmol) and 2,6-dichloropyridine *N*-oxide (2.30 mg, 14 μmol) in 9 mL glass vial in a glove box. The vial was sealed, and the solution was sonicated for 1 minute. Then, the solution was irradiated with a 300 W Xe lamp equipped with a 400 nm long pass filter (Edmund Industrial Optics) to produce the light in the range of $400 \text{ nm} \leq \lambda$ at 20 °C in a custom-made aluminium box with the cooling system. After stopping the reaction, 1.0 μL chlorobenzene was added as the internal standard and [RuBPPy]_{FC} was filtered. The filtrate was used for quantification of the amount of styrene oxide by a Shimadzu GC-2014 with a FID detector equipped with a capillary column (Rtx®-1701). Calibration curves were obtained by sampling known amounts of styrene oxide. In these experiments, the mixed solvent, 5.0% benzene in cyclohexane, was used due to following three reasons; (1) the dielectric constants of these solvents are similar with each other (2.3 for benzene and 2.0 for cyclohexane), (2) [RuBPPy]_{FC} is insoluble and can disperse well in cyclohexane, and (3) the oxidant, 2,6-dichloropyridine *N*-oxide, is soluble in benzene and less soluble in cyclohexane.

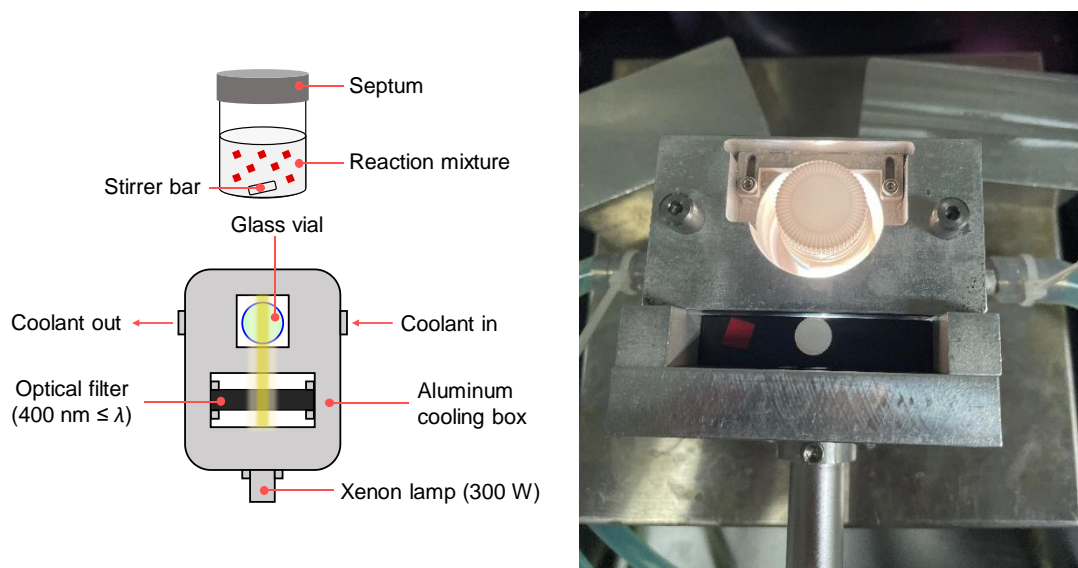


Fig. S11. Custom-made photoreactor. Schematic illustration (A) and a photograph (B) are shown. The coolant was set to 20 °C to maintain a constant sample temperature during measurement.

7.2 The catalytic activity of the filtrate

5.0% benzene in cyclohexane (4.0 mL) solution containing 43 mM styrene was added to [RuBPPy]_{FC} (470 µg, 0.25 µmol) and 2,6-dichloropyridine *N*-oxide (4.1 mg, 25 µmol) in 13.5 mL glass vial in a glove box. The vial was sealed, and the solution was sonicated for 1 minute. Then, the solution was irradiated with a Xe lamp. The catalyst was removed by filtration after 12 h and the filtrate was divided into two parts in the glove box. One was used for quantification and the other was used for an additional 6 h of reaction.

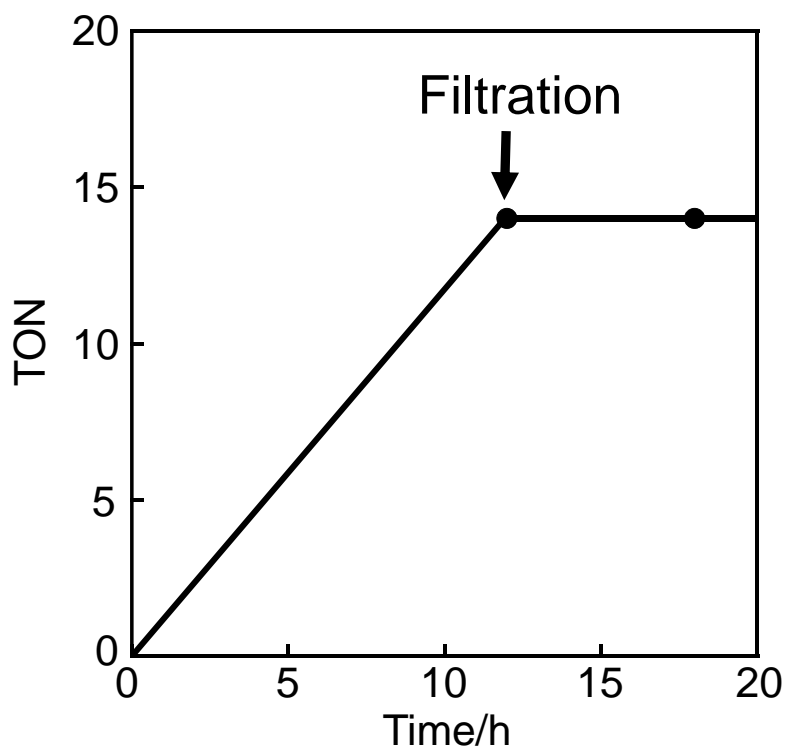


Fig. S12. The catalytic activity of epoxidation in the presence of the catalyst for 12 h and of the filtrate (in the absence of the catalyst) for an additional 6 h.

7.3 Epoxidation of styrene derivatives

Table S5. Epoxidation of styrene derivatives

Entry	R	TON
1	H	19 ± 0.8 ^{a,b}
2	Cl	7.2 ^c
3	Me	18 ^c
4	OMe	15 ^c

[RuBPPy]_{FC} = 0.14 μmol, [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [substance] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 mL) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W). ^aDetermined by GC-FID based on the [RuBPPy]_{FC}, ^bAveraged value over 3 runs with standard deviation, ^cDetermined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard based on the [RuBPPy]_{FC}.

7.4 Light wavelength dependence

We have investigated the catalytic activity of styrene epoxidation upon different light wavelength. In this experiment, special attention has been paid to clarify the role of pyrene unit. As the pyrene units can absorb the light shorter than ca. 450 nm (**Fig. S13**), we have used the following conditions in these experiments; (a) $400 \text{ nm} \leq \lambda$ (standard condition), (b) $400 \text{ nm} \leq \lambda \leq 455 \text{ nm}$ (where the absorption bands of the pyrene unit and the Soret band of the porphyrin moiety exist), and (c) $455 \text{ nm} \leq \lambda$ (where no absorption bands of the pyrene unit exists). As a result, almost no light wavelength dependence on the TON values was confirmed as shown in **Table S6**. The result suggests that the excitation of the porphyrin unit is essential for the catalysis.

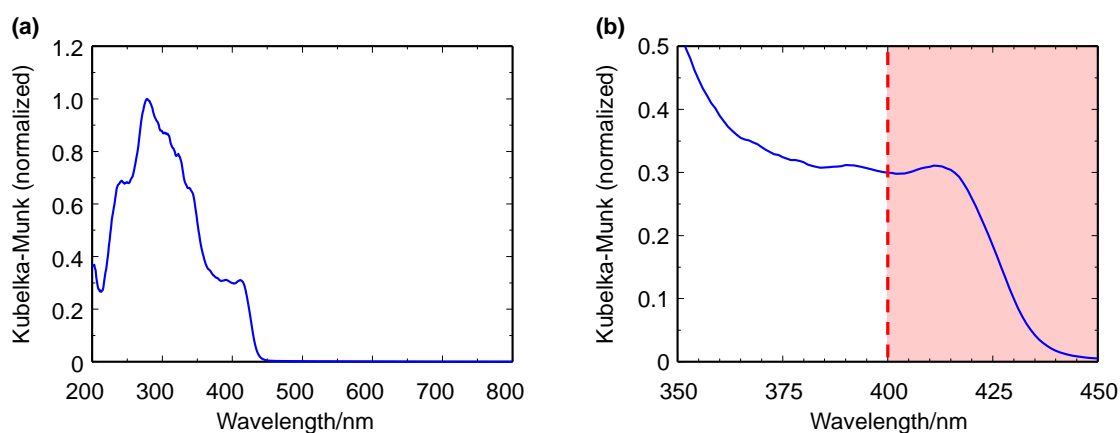


Fig. S13. (a) A diffuse-reflectance UV-vis spectrum of 4-(7-(tert-butyl)pyren-2-yl)benzaldehyde, and (b) an enlarged figure of (a). These figures are reproduced with the permission from ref. S2. **Copyright 2023 American Chemical Society.**

Table S6. Epoxidation of styrene upon different light wavelength

Entry	Wavelength	TON ^a
1	$400 \text{ nm} \leq \lambda$	19 ± 0.8^b
2	$400 \text{ nm} \leq \lambda \leq 455 \text{ nm}$	23
3	$455 \text{ nm} \leq \lambda$	19

[RuBPPy]_{FC} = 0.14 μmol , [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 M) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (300 W). ^aDetermined by GC-FID based on the [RuBPPy]_{FC}. ^bAveraged value over 3 runs with standard deviation.

7.5 Time course

Table S7. Time course of epoxidation of styrene

Time/h	Heterogenous system	Homogenous system
	TON ^a	TON ^a
6	8.0 ± 1	1.3 ± 0.5
18	19 ± 0.8	4.8 ± 0.8
24	24 ± 0.9	8.9 ± 0.4
36	39 ± 3	11 ± 2

[RuBPPy]_{FC} = 0.14 μmol, [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 mL, heterogenous system) and benzene (2.0 mL, homogeneous system) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W). ^aDetermined by GC-FID based on the [RuBPPy]_{FC} and averaged value over 3 runs with standard deviation.

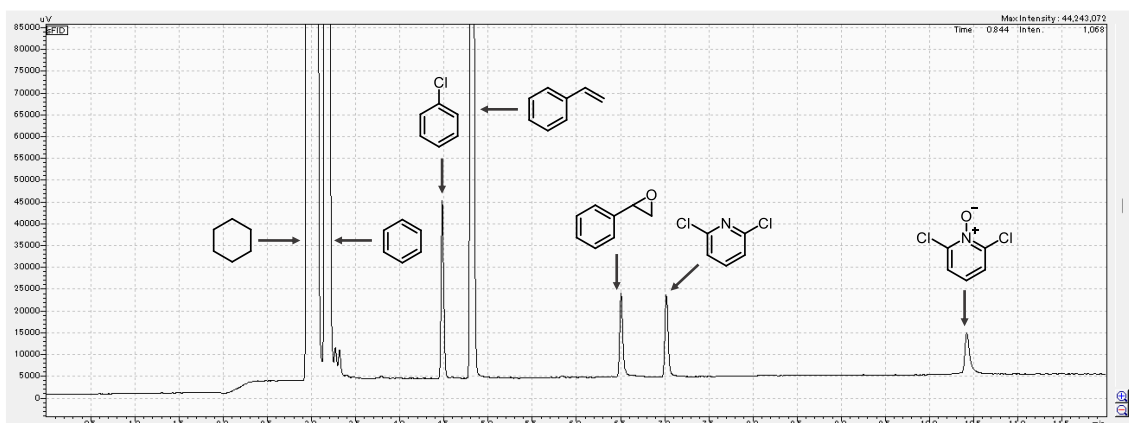


Fig. S14. GC-chart of the epoxidation of styrene for 24 h.

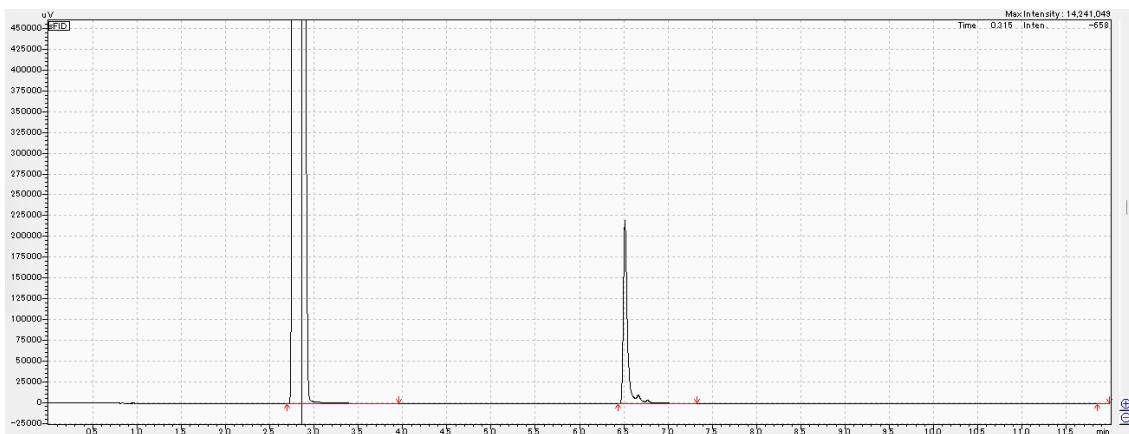


Fig. S15. GC-chart of authentic sample of styrene oxide in acetonitrile.

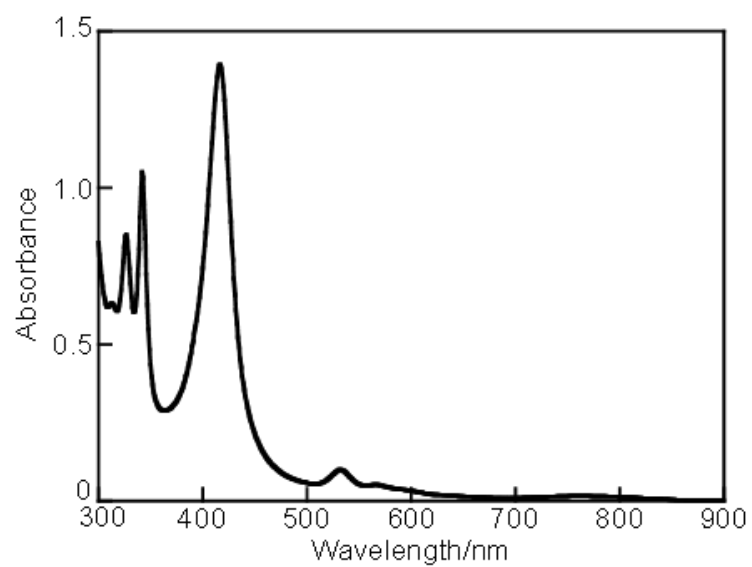


Fig. S16. A UV-vis spectrum of the post catalyst dissolved in CHCl_3 after the epoxidation reaction of styrene for 18 h.

7.6 A Long-term experiment

Table S8. Long-term experiment of [RuBPPy]_{FC} for 96 h

Entry	TON ^a
1	134

[RuBPPy]_{FC} = 0.14 μmol, [2,6-dichloropyridine *N*-oxide] = 28.0 mM (400 equiv.), [styrene] = 86 mM (1240 equiv.) in 5.0% benzene in cyclohexane (2.0 mL) at 20 °C for 96 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W). ^aDetermined by GC–FID based on the [RuBPPy]_{FC}.

7.7 Recycle experiments

Table S9. Recycling tests of **[RuBPPy]_{FC}** for 18 h

Cycle	TON ^a
1	17
2	16
3	16

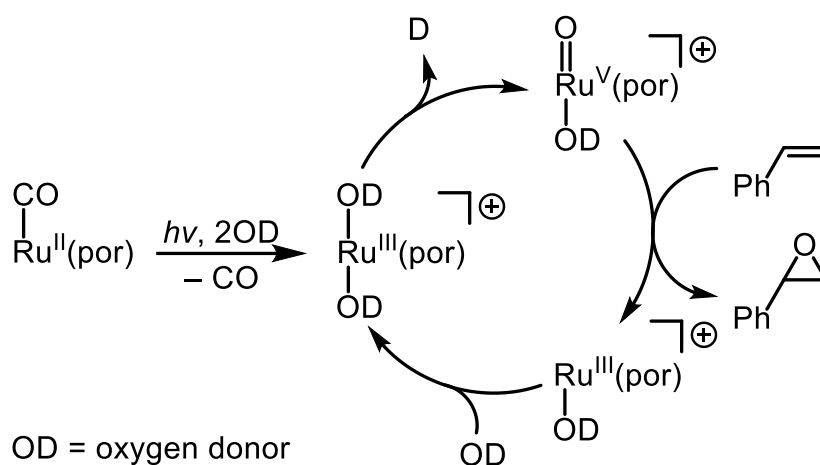
[RuBPPy]_{FC} = 0.78 μ mol, [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (6.0 mL) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm $\leq \lambda$, 300 W).

^aDetermined by GC-FID based on the **[RuBPPy]_{FC}**.

7.8 Proposed mechanism

A possible reaction mechanism for the epoxidation mediated by $[\text{RuBPPy}]_{\text{FC}}$ is proposed (**Scheme S2**). Initially, the reaction of Ru complex with an oxygen donor (OD), 2,6-dichloropyridine *N*-oxide, under the photoirradiated condition affords the one-electron oxidized complex with two OD ligands (**A** in **Scheme S2**) as a key intermediate. The fact that the reaction did not proceed under dark condition (Entry 4 in Table 1) and the previous report^{S17} support that photo-induce decarbonylation is required for the catalysis. Subsequently, Ru(V)-oxo species forms and the formed species reacts with styrene to generate a product and Ru(III)-OD complex. Further reaction of the complex with OD affords **A** to close the catalytic cycle. Note that the Ru(II)-porphyrin carbonyl is known to undergo epoxidation reaction with a Ru(V)/Ru(III) catalytic cycle in the presence of 2,6-dichloropyridine *N*-oxide as an oxidant.^{S18}

Scheme S2 Proposed mechanism of styrene epoxidation with Ru(II)-porphyrin carbonyl complex and 2,6-dichloropyridine *N*-oxide.



8. References

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